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PATENT SPECIFICATION

NO DRAWINGS

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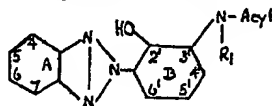
COMPLETE SPECIFICATION

Improvements relating to New Substituted 2-(2'-Hydroxyphenyl)-Benzotriazole Compounds and their use

We, J. R. GEIGY A.—G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns new substituted 2 - (2¹ - hydroxyphenyl) - benzotriazole compounds and processes for the production thereof, their use for the protection of light-sensitive organic materials, i.e. high polymeric materials, their use for the production of UV filters and, as industrial product, the organic material protected from the effect of light with the aid of these compounds.

It has been found that valuable substituted 2 - (2¹ - hydroxyphenyl) - benzotriazole compounds are obtained if a 2 - (2¹ - hydroxyphenyl) - benzotriazole compound containing an acylatable amino group in the 3¹ - position is heated with an acylating agent to form a compound of the general formula



In this formula:
[Price 4s. 6d.]

I

"Acyl" represents an organic acyl radical and R₁ represents hydrogen or an alkyl, alkenyl, cycloalkyl or aralkyl radical which may be substituted by a carboxyl or carboxylic acid ester group; R₁ and "Acyl" together with the amino nitrogen atom can also form a ring and, in this case, R₁ is a carbonyl group or a methylene group possibly substituted by alkyl groups, and wherein the nucleus A can be substituted in the 4-, 5- and 6 - positions by alkyl, alkoxy, carboxyl, carboxylic acid ester, carboxylic acid amide, sulphonic acid amide, alkyl sulphonyl groups or halogens, and the nucleus B can be substituted in the 4¹- and 5¹ - positions by alkyl, cycloalkyl, aralkyl and aryl groups, alkoxy groups or halogens.

Thus, the benzene ring A can contain in the 4-, 5- or 6 - position alkyl groups having 1 to 4 carbon atoms e.g. methyl, ethyl, isobutyl groups, alkoxy groups e.g. methoxy or butoxy groups, halogens e.g. chlorine or bromine, carboxyl groups, carboxylic acid ester groups, preferably carboxylic acid alkyl ester groups such as carbomethoxy, carboethoxy, carbopropoxy or carbobutoxy groups, carboxylic acid or sulphonic acid amide groups possibly aliphatically, cycloaliphatically, araliphatically or aromatically substituted at the nitrogen atom e.g. carboxylic acid or sulphonic acid amide, methylamide, ethylamide, butylamide, cyclohexylamide, benzylamide, di-

[Price 75p]

methanamide, diethylamide, N - methyl - N - cyclohexylamide, γ - methoxypropylamide groups alkylsulphonyl groups e.g. alkyl substituted carboxylic acid amide and alkyl substituted methylsulphonyl or ethylsulphonyl groups, sulphonic acid amide groups, which substituents together with the nitrogen atom and with the possible inclusion of a further hetero atom form a saturated heterocyclic ring e.g. carboxylic acid and sulphonic acid piperide or morpholide groups. The benzene ring B can be substituted in the 4¹- and 5¹- positions by alkyl groups e.g. methyl, ethyl, tert. butyl groups; aralkyl groups e.g. benzyl groups; cycloalkyl groups e.g. cyclohexyl groups or aryl groups e.g. phenyl groups, alkoxy groups e.g. methoxy, ethoxy, propoxy, isopropoxy or n - butoxy groups or halogens e.g. chlorine or bromine.

In the group $\begin{array}{c} R_1 \\ | \\ -N- \end{array}$ Acyl, "Acyl is a radi-

cal of the formula $\begin{array}{c} Y \\ || \\ -X-R_2 \end{array}$ wherein X is a

carbon atom or the radical $\begin{array}{c} | \\ -S=O \\ || \end{array}$ and Y is

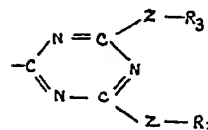
an oxygen atom or, if X is a carbon atom, also a sulphur atom, or Y can be an imino group which with X and R_2 forms an s - triazine or pyrimidine ring. R_2 represents an alkyl, alkenyl, cycloalkyl, aralkyl or an aryl group whilst the aryl group can be substituted, e.g. by halogen atoms, alkoxy, alkyl, free or modified carboxyl groups and, particularly if X is a carbon atom, R_2 represents also an alkyl group which can be further substituted by halogen atoms, etherified mercapto groups, free or etherified hydroxy groups, primary, secondary or tertiary amino groups and free or modified carboxyl groups, or, if X is a carbon atom, R_2 also represents hydrogen, or an alkoxy, alkenyloxy, cycloalkyloxy, aralkyloxy or an aryloxy group whilst the aryl radical of the aralkoxy or aryloxy group can be substituted e.g. by alkyl, alkoxy groups or halogen atoms and the alkoxy group can be substituted by alkoxy or alkylmercapto groups, or an amino group which can be substituted at the nitrogen atom by one or two identical or different alkyl, alkenyl, cycloalkyl, aralkyl or aryl groups, or an imino group of a saturated monocyclic heterocycle, or, if R_1 and R_2 are linked together, together with X and R_1 , it represents the remainder of a lactam or dioxopyrrolidine ring.

In every case, the olefinic double bond of the alkenyl group which may be present is separated from the next hetero atom by at least one carbon atom and the hetero atoms bound to

saturated carbon atoms are separated from the next hetero atom by at least one further carbon atom.

Preferably "acyl" represents the following groups; the preferred number of carbon atoms of this group is given in brackets.

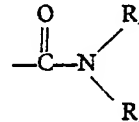
a) An s - triazinyl radical of the formula



wherein Z represents an imino or an alkyl-imino group (C_{1-6}), an oxygen or sulphur atom, and R_1 represents an alkyl group (C_{1-12}), cycloalkyl group (C_{3-8}), or an aralkyl group (C_{7-12}), whilst R^3 together with an alkyl-imino group can form a 5 to 7 membered, saturated heterocyclic ring (and the whole group contains at most 25 carbon atoms),

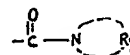
b) a pyrimidyl radical which contains in the ring at most one CH— group and which is substituted at the other carbon atoms by chlorine and at most one ZR_1 — group (and the whole group contains at most 17 carbon atoms),

c) a carbamoyl radical of the formula



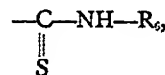
wherein R_1 and R_2 independently of each other represent hydrogen or an R_6 — group (R_1 and R_2 together contain at most 19 carbon atoms), in such an R_6 — group or hereafter R_6 represents an alkyl group (C_{1-18}), an alkenyl group (C_{3-8}), a cycloalkyl group (C_{3-8}), an aralkyl group (C_{7-12}), or an aryl group (C_{6-10}), which can be substituted in particular by halogen atoms, alkoxy, alkyl, free or modified carboxyl groups,

d) a carbamoyl radical of the formula

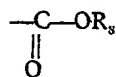


wherein R_7 represents an alkylene radical (C_{2-6}) or an oxalkylene radical (C_{2-6}) which together with the nitrogen atom forms a 5 to 7 membered saturated heterocyclic ring,

e) a thiocarbamoyl radical of the formula



f) a carbonic acid monoester radical of the formula



- 5 wherein R_8 has the same meaning as R_6 and in addition, it represents an alkoxyalkyl radical (C_{7-10}), a halogenalkyl radical (C_{1-2}), or an alkylmercaptoalkyl radical (C_{3-10}),

g) a carboxylic acid radical of the formula



- 10 wherein R_9 has the same meaning as R_8 and in addition it represents hydrogen or an alkenyl radical (C_{6-13}), a carboxyalkyl radical (C_{2-10}), a carboxyaryl radical (C_7), carboxyalkenyl radical (C_{4-6}), a carbalkoxyalkyl radical (C_{3-11}), a carboxyalkoxyalkyl radical (C_{8-9}), a carboaralkoxyalkyl radical (C_{8-14}), a carboaryloxyalkyl radical (C_{8-14}), an R_6 - O - alkyl radical (C_{2-22}), an R_6 - S - alkyl radical

(C_{2-22}), an R_4 - N - alkyl radical (C_{2-22}), an R_5 - alkylene radical (C_{4-9}) or an oxalkylene radical (C_{4-9}), or

- 20 h) a sulphonic acid radical of the formula $\text{—SO}_2\text{R}^1$ wherein R^1 has the meaning given for R_6 .

- 25 If R_1 to R_9 are aryl radicals then they are preferably monocyclic.

- R_1 is preferably hydrogen, an unsubstituted alkyl group (C_{1-18}), a carboxyalkyl group (C_{2-9}), a carbalkoxyalkyl group (C_{2-14}), a cycloalkyl group (C_{5-6}) or an aralkyl group (C_{7-12}).

- 30 If R_1 and R_2 are bound together, R_1 is preferably a carbonyl or a methylene group and R_2 is a 1,2 - ethylene group. Preferably R_1 and the "acyl" radical together contain at most 26 carbon atoms, at most 5 nitrogen atoms, at most 4 oxygen atoms and at most 2 sulphur atoms.

- 35 Benztriazole compounds which absorb at particularly long wave lengths are obtained if there are acidifying substituents in the ring A and/or basifying substituents in the 5¹-position. Benztriazole compounds having particularly high molar extinction in the range of 330—350 $m\mu$ are obtained if there are basifying substituents in the 5- and/or 4¹ - position. Sometimes the molar absorption in the range of 300 $m\mu$ is promoted by further substituted alkyl substituents in the 5¹ - position. Examples of basifying substituents are alkoxy groups e.g. the methoxy, isopropoxy, cyclohexyloxy and

benzyloxy group; examples of acidifying substituents are the alkylsulphonyl groups e.g. the methyl and ethyl sulphonyl group, sulphonic acid amide groups e.g. the sulphonic acid methylamide, butylamide and cyclohexylamide group, as well as the carboxyl group and its esters or amides.

Naturally, typical dyestuff groups, e.g. aromatic azo groups, anthraquinone groups containing auxochromes or phthalocyanine groups, are to be excluded as substituents from the benztriazole compounds according to the invention.

The 2 - (2¹ - hydroxyphenyl) - benztriazole compounds having an acylatable amino group in the 3¹ - position and which can be further substituted as defined for A and B in formula I, which are used as starting materials according to the invention, are obtained by methods known per se, for example by coupling a possibly further substituted 2 - nitrobenzene diazonium compound with a 2 - acylamino - 1 - hydroxybenzene coupling in *o* - position to the hydroxyl group, and reducing the 2 - nitroazo compound obtained to the triazole compound, for example, with zinc dust in alkaline medium, and saponifying the acylamino group to the amino group.

2 - (2¹ - hydroxyphenyl) - benztriazole compounds substituted in the 5¹ - position and having a free 3¹ - position can also be nitrated and the 2 - (2¹ - hydroxy - 3¹ - nitrophenyl) - benztriazole compounds obtained reduced to the 3¹ - amino compound.

To introduce the "acyl" radical e.g. the carboxylic acid radical of the formula $R_2\text{—CO—}$ into the starting materials usable according to the invention acylating agents are used, e.g. anhydrides, esters, e.g. esters of alkanols having 1 to 6 carbon atoms, and preferably, halides, in particular chlorides, or ketenes of carboxylic acids corresponding to $R_2\text{—CO—}$; to introduce a carbonic acid monoester radical of the formula $R_8\text{—OCO—}$, a sulphonic acid radical of the formula $R_6\text{—SO}_2\text{—}$ and a cyclic carbonic acid imide radical, in particular a 1,3,5 - triazinyl - (2) radical, in each case the halides, chiefly the chlorides, of the corresponding acids are used.

To introduce a carbamoyl or thiocarbamoyl radical either the halides of the corresponding acids are used, or advantageously, isocyanates or mustard oils, for example, phenyl isocyanate or phenyl mustard oil.

The 2 - (2¹ - hydroxyphenyl) - benztriazole compound containing an acylatable amino group in the 3¹ - position is reacted with the acylating agent by heating, possibly in inert organic solvents e.g. in halogenated or nitrated aromatic hydrocarbons, for example in benzene, toluene, chlorobenzene or nitrobenzene, or in a tertiary amine e.g. in pyridine or diethyl aniline. In every case, care should be

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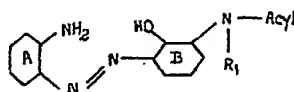
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taken that the hydroxyl group in the 2¹ - position is not acylated. This is done by performing the reaction in a weakly acid to weakly alkaline medium.

5 If the compounds of formula I contain reactive groups, these can subsequently be converted by further reactions into other groups. Thus, for example, mobile halogen in halogen fatty acid amide groups can be exchanged for the corresponding alkoxy, mercaptide, amino or cyano group by reaction with alcohols, mercaptans, primary or secondary amines or alkali cyanides; or carboxyl or sulphonic acid groups can be converted by way of the acid chloride into corresponding acid ester or amide groups; or alcohols, mercaptans, amines or hydrocyanic acid can be added at suitable double bonds.

20 Examples of such subsequent modifications are the replacement of the chlorine atom in 2 - (2¹ - hydroxy - 3¹ - β chloropropionylamino - 5¹ - methylphenyl) - benztriazole by diethylamine, cyclohexylamine, benzylamine and N - methylcyclohexylamine, to form 2 - (2¹ - hydroxy - 3¹ - β - diethylaminopropionylamino - 5¹ - methyl - phenyl) - benztriazole, 2 - (2¹ - hydroxy - 3¹ - β - cyclohexylaminopropionylamino - 5¹ - methylphenyl) - benztriazole, 2 - (2¹ - hydroxy - 3¹ - β - benzylaminopropionylamino - 5¹ - methylphenyl) - benztriazole and 2 - (2¹ - hydroxy - 3¹ - β - methylcyclohexylaminopropionylamino - 5¹ - methylphenyl) - benztriazole, or the addition of octylmercaptan to 2 - (2¹ - hydroxy - 3¹ - acryloylmethylamino - 5¹ - chlorophenyl) - 5 - ethylbenztriazole to form 2 - (2¹ - hydroxy - 3¹ - β - octylmercaptopropionylmethylamino - 5¹ - chlorophenyl) - 5 - ethylbenztriazole.

40 Another process for the production of 2 - (2¹ - hydroxyphenyl) - benztriazole compounds substituted according to the invention consists in oxidising, by methods known per se, a 2-amino - 2¹ - hydroxy - 3¹ - acylamino - 1,1¹ - azobenzene compound of the general formula II



II

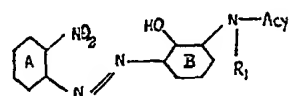
wherein "Acyl", R₁, A and B have the meanings given in formula I, to form a compound of formula I.

50 o - Aminoazobenzene compounds usable as starting materials and which correspond to formula II are obtained for example by coupling a 2 - hydroxy - 3 - nitrobenzene diazonium compound with an aminobenzene coupling in o - position to the amino group, then reducing the nitro group by the usual methods and acylating the amino group formed.

It is also possible for the hydroxyl group in formula II to be esterified, particularly by sulphonic acids. The hydroxyl group can be liberated by mild hydrolysis after or during the oxidation.

The o - aminobenzene compound of formula II is oxidised to the triazole compound of formula I by the usual methods, e.g. with salts of divalent copper in alkaline medium.

A further process for the production of 2 - (2¹ - hydroxyphenyl) - benztriazole compounds substituted according to the invention consists in reducing, by methods known per se, a 2 - nitro - 2¹ - hydroxy - 3¹ - acylamino - 1,1¹ - azobenzene compound of the general formula III

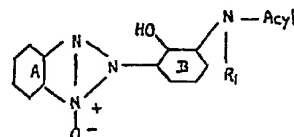


III

wherein "Acyl", R₁, A and B have the meanings given in formula I, to form a compound of formula I. Compounds of the formula III are obtained, e.g. by coupling a possibly further substituted 2 - nitrobenzene diazonium compound with a 2 - acylamino - phenol coupling in o - position to the hydroxyl group.

The o - nitroazobenzene compound of formula III is reduced to the triazole compound of formula I in the usual way, e.g. with zinc dust in alkaline medium.

The 2 - (2¹ - hydroxy - 3¹ - acylaminophenyl) - benztriazole oxides obtained as intermediates in the reduction with zinc dust of formula IIIa

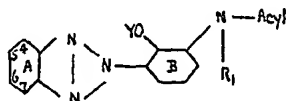


IIIa

can be isolated in substance by reduction with hydrosulphite. These triazole oxides can be converted into the desired triazole compounds by catalytic reduction and also by zinc dust reduction.

Another process for the production of 2 - (2¹ - hydroxyphenyl) - benztriazole compounds substituted according to the invention consists in dealkylating the alkoxy group in a 2 - (2¹ - alkoxy - 3¹ - acylaminophenyl) - benztriazole compound or hydrolysing the acloxy group in a 2 - (2¹ - acloxy - 3¹ - acylaminophenyl) - benztriazole compound; both processes are performed by methods known per se.

The 2 - (2¹ - alkoxy - 3¹ - acylamino-phenyl)- and 2 - (2¹ - acyloxy - 3¹ - acylamino-phenyl) - benztriazole compounds usable according to the invention as starting materials correspond to the general formula IV



IV

wherein "Acyl", R₁, A and B have the meanings given in formula I and Y represents an alkyl radical, e.g. the methyl or ethyl radical or an acyl radical, e.g. the acetyl or benzoyl radical.

They are obtained, for example, by coupling a 2 - alkoxy - 3 - acylamino- or 2 - acyloxy - 3 - acylamino- benzene diazonium compound with an aminobenzene coupling in *o* - position to the amino group and then oxidising to form the corresponding triazole.

The dealkylation is performed preferably with aluminium chloride in benzene but it can possibly also be performed by hydrogenolysis or benzyl ethers in the presence of Raney nickel; the saponification is performed by the usual methods in aqueous medium.

Depending on the way in which they are substituted, the new substituted 2 - (2¹ - hydroxy - 3¹ - acylaminophenyl) - benztriazole compounds of formula I are colourless to pale yellowish coloured and they absorb ultraviolet light. Compared with previously known compounds of similar constitution they are an improvement both in absorption of long wave UV light, in the stabilising effect on organic material which is sensitive to UV light and they are distinguished by less volatility. They are incorporated into light-sensitive carriers in small amounts of 0.001—5% by weight, in particular in amounts of 0.01—1% by weight of the carrier.

The main carriers for the new compounds of formula I are polymers, chiefly completely synthetic polymers, e.g. addition polymers, in particular polymers of ethylenically unsaturated monomers, e.g. polyvinyl chloride, polyvinylidene chloride, styrene polymers, diene polymers, as well as their copolymers, polyethylene, polypropylene, polyacryl compounds, in particular polymethylmethacrylate or polyacrylonitrile, also condensation polymers e.g. polyesters, e.g. polyethylene glycol terephthalates, or polyamides, e.g. polycaprolactam, or also mixed polymers e.g. polyester resins; also natural polymers or synthetic modifications thereof such as, e.g. cellulose, cellulose esters and ethers, and proteins. The molecular weight of the polymers mentioned above plays a subsidiary role as long as it lies within the margins

necessary for the characteristic mechanical properties of the polymers concerned. Depending on the polymers it can be between 1000 to several millions. The new substituted 2 - (2¹ - hydroxy - 3¹ - acylaminophenyl) - benztriazole compounds are incorporated, e.g. into these polymers — depending on the type of polymers — by working in at least one of these compounds and, possibly, further additives e.g. plasticisers, antioxidants, heat stabilisers and pigments, into the melts by the methods usual in the industry before or during moulding, or they are incorporated by dissolving in the corresponding monomers before polymerisation or by dissolving the polymers and additives by adding solvents and then evaporating off the latter. The new substituted 2 - (2¹ - hydroxy - 3¹ - acylaminophenyl) - benztriazole compounds can also be drawn from baths, e.g. aqueous dispersions, onto films or threads.

The light-sensitive materials can also be protected from the effect of light by painting them with a protective coating containing at least one compound as defined of formula I, for example, with a lacquer, or they can be covered — advantageously with films — with coverings which contain such actinic agents. In both these cases, the amount of actinic agent added is advantageously 10—30% by weight (calculated on the protective coating material) for protective coatings or films of less than 0.01 mm thickness and 1—10% by weight for those of 0.01 to 0.1 mm thickness. The benztriazole derivatives according to the invention are all the more valuable the more colourless they are as otherwise they lend to the finished product a yellow shading.

Those benztriazole compounds are particularly suitable in non-polar polymers which, apart from the hydroxyl group present as defined, contain as few groups as possible with mobile hydrogen atoms e.g. secondary carboxylic or sulphonic acid amide groups. In this case, generally products having a low melting point are preferred because of their solubility.

In general, it is recommended that the possible use of a specific product be estimated by solubility trials. For example, if the product is difficultly soluble, even hot, in the solvents known for the polymers to be protected, then unfavourable results in this polymer are to be expected.

For certain uses, particularly when warm chips are to be powdered, those benztriazole compounds are particularly valuable which melt at a temperature higher than the polymer fuses and, in spite of this, are sufficiently soluble in melted polymers.

The following Examples illustrate the invention. Where not otherwise stated, parts are given as parts by weight. The temperatures are in degree Centigrade. The relationship of parts by weight to parts by volume is as that of kilogrammes to litres.

EXAMPLE 1

12 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole are heated in 150 parts by volume of pyridine to 80° and 8 parts of heptane carboxylic acid chloride are added dropwise at this temperature to this solution. After half an hour, a little animal charcoal is added, the mixture is filtered hot and the residue is washed with hot pyridine. The filtrate is diluted with water, the precipitate formed is filtered off under suction, washed with water and crystallised from methanol. 13 Parts of 2 - (2¹ - hydroxy - 3¹ - heptane carboxylic acid amido - 5¹ - methylphenyl) - benztriazole (M.P. 110°) are obtained.

The following compounds are obtained by the same method on using an equivalent amount of the corresponding acid chloride instead of the heptane carboxylic acid chloride:

- 2 - (2¹ - hydroxy - 3¹ - stearoylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - oleoylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - cyclohexane carboxylic acid amido - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - phenylacetamido - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - methacryloylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - cyclopentane carboxylic acid amido - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹,β - phenylpropionylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - chloroacetamido - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - β - methoxypropionylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - γ - chlorobutyrylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - β - butylmercaptopyrionylamino - 5¹ - methylphenyl) - benztriazole.

The 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole used as starting material is produced as follows:

225 Parts of 2 - (2¹ - hydroxy - 5¹ - methylphenyl) - benztriazole are dissolved at room temperature in 2000 parts by volume of 80% sulphuric acid and the solution obtained is cooled to 10°. A mixture of 80 parts by volume of concentrated nitric acid (d=1.4) and 80 parts by volume of water are added dropwise at this temperature within 4 hours. The reaction mixture is then poured onto ice, the yellow precipitate is filtered off under suction, washed neutral with water and dried. 260 Parts of 2 - (2¹ - hydroxy - 3¹ - nitro - 5¹ - methylphenyl) - benztriazole are obtained which, when recrystallised from benzene, melts at 176°.

135 Parts of the 2 - (2¹ - hydroxy - 3¹ - nitro - 5¹ - methylphenyl) - benztriazole so obtained are dissolved in 800 parts by volume of boiling ethylene glycol. 80 Parts of hydrazine hydrate are added dropwise to the solution obtained, the addition being made under reflux and within 2 hours. After cooling, the voluminous, yellow precipitate is filtered off under suction, washed with a little methanol and dried. 108 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole are obtained. M.P. 220°.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 2

35 Parts of moist *o* - nitro - azo dyestuff, obtained by coupling 13.8 parts of diazotised *o* - nitroaniline with 16.5 parts of 2 - acetamido - 4 - methylphenol, are suspended in 200 parts by volume of 3 N caustic soda lye. After the addition of 25 parts of zinc dust, the whole is stirred at 0—5° until decolouration occurs, acidified with hydrochloric acid, filtered and the product is crystallised from ethanol. 2 - (2¹ - hydroxy - 3¹ - acetamido - 5¹ - methylphenyl) - benztriazole (M.P. 176°) is obtained.

If 2.4 1 dichloro - 6 - nitroaniline is used instead of the simple nitroaniline, 2 - (2¹ - hydroxy - 3¹ - acetamido - 5¹ - methylphenyl) - 4,6 - dichlorobenztriazole is obtained by the same method.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 3

12 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole in 150 parts by volume of pyridine are heated to 60° and a mixture of 7 parts of benzoyl chloride and 20 parts by volume of pyridine is slowly added dropwise at this temperature to the solution formed. After half an hour, the solution is poured into water, the precipitate is filtered off under suction, dried and crystallised twice from benzene. 11 Parts of 2 - (2¹ - hydroxy - 3¹ - benzoylamino - 5¹ - methylphenyl) - benztriazole are obtained. M.P. 214°.

If, instead of the benzoyl chloride, an equivalent amount of the corresponding acid chloride is used, then the following substances are obtained:

- 2 - (2¹ - hydroxy - 3¹ - *p* - methoxybenzoylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - *p* - chlorobenzoylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - *o* - methylbenzoylamino - 5¹ - methylphenyl) - benztriazole,

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 4

12 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole are dissolved in 200 parts by volume of glacial acetic acid with the addition of 7.5 parts of sodium acetate. After the addition of 10 parts of *p*-toluene sulphonic acid chloride, the whole is refluxed for 1 hour, diluted with water while still hot, cooled, filtered under suction and the product is recrystallised from chlorobenzene. 11.5 Parts of 2 - (2¹ - hydroxy - 3¹ - *p*-toluene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole are obtained. M.P. 228°.

If, instead of the *p*-toluene sulphonic acid chloride, an equivalent amount of benzene sulphonic acid chloride, *p*-chlorobenzene sulphonic acid chloride or methoxybenzene sulphonic acid chloride is used, then 2 - (2¹ - hydroxy - 3¹ - benzene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole or 2 - (2¹ - hydroxy - 3¹ - *p*-chlorobenzene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole or 2 - (2¹ - hydroxy - 3 - *p*-methoxybenzene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole respectively is obtained.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 5

13 Parts of 2-(2¹-hydroxy-3¹-amino-5¹-chlorophenyl) - benztriazole (M.P. 206°), 100 parts by volume of chlorobenzene and 6 parts of phenyl isocyanate are refluxed for 1 hour. After cooling, the precipitate is filtered off, under suction, washed with benzene and crystallised from glacial acetic acid. 13.5 Parts of 2 - (2¹ - hydroxy - 3¹ - phenyl - carbamoyl amino - 5¹ - chlorophenyl) - benztriazole are obtained. M.P. 257°.

The 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - chlorophenyl) - benztriazole is obtained by nitration of 2 - (2¹ - hydroxy - 5¹ - chlorophenyl) - benztriazole and reduction of the 3¹ - nitro compound (M.P. 191°) so obtained by the method described in the second paragraph of Example 1.

If, instead of the 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - chlorophenyl) - benztriazole, an equivalent amount of a corresponding aminophenylbenztriazole is used, then the following products are obtained:

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl-amino - 5¹ - α - phenylethylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - amino - 5¹ - 1¹¹ - methylcyclohexyl - phenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - amino - 5¹ - benzylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoylcyclohexylamino - 5¹ - methylphenyl) - benztriazole.

The end products mentioned can be used as

UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 6

2.4 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole are stirred with 30 parts of chlorobenzene and 1.3 parts of dimethyl aniline. 1.8 Parts of β - butylmercaptopropionyl chloride are slowly added to the suspension formed and the resultant mixture is brought to the boil under reflux while stirring well and refluxed for half an hour. It is then cooled and the reaction product is poured into water. The chlorobenzene is removed by steam distillation whereupon, after cooling, the 2 - (2¹ - hydroxy - 3¹ - β - butylmercaptopropionyl - amino - 5¹ - methylphenyl) - benztriazole remains as crystals which solidify into a cake. After removal of the water the substance is dried in a water jet vacuum and afterwards recrystallised several times from ligroin. It then melts at 151°. Also mixtures of chlorobenzene and ligroin can be used as recrystallisation agents.

On using an equivalent amount of the corresponding acid chloride instead of the β - butylmercaptopropionic acid chloride, the following products are obtained by the same method:

2 - (2¹ - hydroxy - 3¹ - phenoxyacetyl-amino - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - β - ethoxypropionyl-amino - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - methoxyacetyl-amino - 5¹ - methylphenyl) - benztriazole,

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 7

15 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - cyclohexylphenyl) - benztriazole (M.P. 192°) and 5 parts of succinic acid anhydride in 200 parts by volume of chlorobenzene are refluxed for 2 hours. The precipitate is filtered off under suction and crystallised from glacial acetic acid. 16.5 Parts of 2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl-amino - 5¹ - cyclohexylphenyl) - benztriazole are obtained. M.P. 201°.

The 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - cyclohexylphenyl) - benztriazole is obtained by nitration of 2 - (2¹ - hydroxy - 5¹ - cyclohexylphenyl) - benztriazole and reduction of the 3¹ - nitro compound obtained (M.P. 173°) by the methods described in the second and third paragraphs of Example 1.

If the same components are refluxed in an apparatus fitted with a water separator and 0.2 parts of *p*-toluene sulphonic acid chloride are added to the mixture then water soon begins to separate. The mixture becomes homogeneous and the reaction is interrupted when no more water is given off. On cooling, the 2 - (2¹ - hydroxy - 3¹ - (2¹¹, 5¹¹ - diketo-

pyrrolidinyl - (1¹¹) - 5¹ - cyclohexylphenyl) - benztriazole crystallises out.

If instead of the succinic acid anhydride, an equivalent amount of phthalic acid anhydride or maleic acid anhydride is used, then in the same manner are obtained:

2 - (2¹ - hydroxy - 3¹ - *o* - carboxybenzoyl-amino - 5¹ - cyclohexylphenyl) - benztriazole,

10 2 - (2¹ - hydroxy - 3¹ - β - carboxyacrylyl-amino - 5¹ - cyclohexylphenyl) - benztriazole or, on splitting off of water,

2 - (2¹ - hydroxy - 3¹ - (2¹¹,5¹¹ - diketo - pyrrolinyl - (1¹¹)) - 5¹ - cyclohexylphenyl) - benztriazole.

15 The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

20 EXAMPLE 8

a) 3.9 Parts of 2 - [2¹ - hydroxy - 3¹ - (4¹¹, 6¹¹ - dichloro - 1¹¹,3¹¹,5¹¹ - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole (M.P. 223°) and 6 parts of *n* - dibutylamine in 50 parts by volume of ethylene glycol monomethyl ether are refluxed for 12 hours. After dilution with 50 parts by volume of water and cooling, the 2 - [2¹ - hydroxy - 3¹ - (4¹¹,6¹¹ - bis - dibutylamino - 1¹¹,3¹¹,5¹¹ - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] benztriazole precipitates. After once recrystallising from ethanol, the product melts at 106°.

b) 2.4 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole and 3.7 parts of 2,4 - bis - (dibutylamino) - 6 - chloro - *s* - triazine in 20 parts by volume of *o* - dichlorobenzene are refluxed for 2 hours. After evaporating off the solvent, the residue is taken up in 50 parts by volume of ethanol and 5 parts of sodium acetate are added to this solution. The precipitate formed is filtered off under suction and recrystallised from ethanol. The product obtained is identical with the 2 - [2¹ - hydroxy - 3¹ - (4¹¹,6¹¹ - bis - dibutylamino - 1¹¹,3¹¹,5¹¹ - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole obtained according to a). Melting point when mixed with the product according to a): 106°.

If, instead of 2,4 - bis - (dibutylamino) - 6 - chloro - *s* - triazine, 2,4 - bis - (cyclohexyloxy) - 6 - chloro - *s* - triazine, 2 - benzyloxy - 4 - methyloxy - 6 - chloro - *s* - triazine,

55 2,4 - bis - (octylmercapto) - 6 - chloro - *s* - triazine, 2,4 - bis - (butylmercapto) - 6 - chloro - *s* - triazine,

4 - *N* - methylcyclohexylamino - 2,5,6 - trichloropyrimidine, or 60 4 - butylmercapto - 2,6 - dichloropyrimidine is used, then

2 - [2¹ - hydroxy - 3¹ - (4¹¹,6¹¹ - dicyclohexyloxy - *s* - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole,

2 - [2¹ - hydroxy - 3¹ - (4¹¹ - benzyloxy - 6¹¹ - methoxy - *s* - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole,

2 - [2¹ - hydroxy - 3¹ - (4¹¹,6¹¹ - dioctylmercapto - *s* - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole,

2 - [2¹ - hydroxy - 3¹ - (4¹¹,6¹¹ - dibutylmercapto - *s* - triazinyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole,

2 - [2¹ - hydroxy - 3¹ - (4¹¹ - *N* - methylcyclohexylamino - 2¹¹,5¹¹ - dichloropyrimidyl - (6¹¹) - amino) - 5¹ - methylphenyl] - benztriazole, or

2 - [2¹ - hydroxy - 3¹ - (4¹¹ - butylmercapto - 5¹¹ - chloropyrimidyl - (2¹¹) - amino) - 5¹ - methylphenyl] - benztriazole

is obtained.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 9

27.4 Parts of 2 - (2¹ - *p* - toluene sulphonyloxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole (M.P. 209°, produced by reacting 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole with 2 equivalents of *p* - toluene sulphonyl chloride in an alkaline medium), and 200 parts by volume of a mixture of 2 *N* caustic soda lye and ethanol (1:1) are refluxed for 30 minutes. After cooling, the yellow solution is acidified with dilute hydrochloric acid, the precipitate formed is filtered off under suction and crystallised from chlorobenzene. 2 - (2¹ - hydroxy - 3¹ - *p* - toluene sulphonyloxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole is obtained, M.P. 228°.

If, instead of 2 - (2¹ - *p* - toluene sulphonyloxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - benztriazole, 2 - (2¹ - *p* - toluene sulphonyloxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - 5 - methylbenztriazole is used and otherwise the same procedure is followed, then 2 - (2¹ - hydroxy - 3¹ - *p* - toluene sulphonyloxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - 5 - methylbenztriazole is obtained.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 10

13.7 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - chlorobenztriazole, 4.7 parts of chlorocarbonic acid methyl ester and 6.5 parts of *N,N* - dimethyl aniline in 200 parts by volume of chlorobenzene are refluxed for 1 hour. After cooling, the solution is filtered, the solvent is almost completely distilled off and the product which crystallises out is recrystallised from benzene. 2 - (2¹ - hydroxy - 3¹ - carbomethoxyamino - 5¹ - methylphenyl) - 5 - chloro-

benztriazole is obtained. M.P. 181°.

By the same process on using an equivalent amount of the corresponding aminophenyl-benztriazole instead of the 5 - chlorobenztriazole derivative mentioned above, the following products are obtained:

- 2 - (2¹ - hydroxy - 3¹ - carbomethoxyamino - 5¹ - cyclopentylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbomethoxycyclohexylamino - 5¹ - methylphenyl) - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbomethoxybenzylamino - 5¹ - methylphenyl) - 4 - chlorobenztriazole, or
- 2 - (2¹ - hydroxy - 3¹ - carbomethoxyamino - 5¹ - bromophenyl) - benztriazole - 5 - carboxylic acid butyl ester.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 11

The still moist dyestuff, produced by coupling the diazo compound of 44.6 parts of 2 - tosyloxy - 3 - tosylamino - 5 - methylaniline (obtained by reacting 2 - amino - 6 - nitro - 4 - methylphenol with 2 equivalents of *p* - toluene sulphonyl chloride and then reducing according to Béchamp), and 13.7 parts of 3 - methoxy - 4 - methyl aniline in acetic acid solution, and 100 parts by volume of ethylene glycol monomethyl ether in 30 parts by volume of concentrated caustic soda lye are heated in a water bath until the content of free alkali is no longer reduced over a period of 15 minutes. The solution obtained is then acidified while cooling well with 5 N - hydrochloric acid whereupon the 2 - hydroxy - 2¹ - amino 3 - tosylamino - 4¹ - methoxy - 5,5¹ - dimethyl - 1,1¹ - azobenzene precipitates. The dyestuff is filtered off under suction, dissolved in 500 parts by volume of pyridine and, at 50—60°, 100 parts by volume of 2 molar copper sulphate solution are added. The mixture obtained is heated in a boiling water bath and stirred until the dyestuff is no longer coloured. 200 Parts by volume of concentrated ammonia are then added and the pyridine is distilled off in steam. The product which separates out is dissolved in a mixture of equal volumes of ethanol and 2 N caustic soda lye and decoppered with sodium sulphide solution. The copper sulphide is filtered off and the filtrate is slowly acidified at 70—80° whereupon the 2 - (2¹ - hydroxy - 3¹ - *p* - toluene sulphonic acid amido - 5¹ - methylphenyl) - 5 - methoxy - 6 - methylbenztriazole separates out in crystalline form. The end product can be used as UV absorber and is suitable, depending on its solubility properties, as a stabiliser for various synthetic materials.

EXAMPLE 12

2.7 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - chlorobenztriazole

(M.P. 209°, produced from 2 - (2¹ - hydroxy - 5¹ - methylphenyl) - 5 - chlorobenztriazole (M.P. 109°) by nitration and reduction of the nitro compound obtained as described in Example 1), 100 parts of chlorobenzene, 2 parts of dimethyl aniline and 2 parts of chlorocarbonic acid cyclohexyl ester are mixed, in the order given, while stirring well at room temperature and the mixture is slowly heated and then kept for 1 hour under reflux. The whole is stirred overnight at room temperature and the reaction mixture is then filtered. The residue is first washed with a little benzene and the filtrate obtained is combined with the main filtrate. This is then concentrated and the residue is combined with the previous filter residue. The somewhat greasy mass is pasted well with a 1:1 mixture of 1 N hydrochloric acid and methanol and filtered under suction, which pasting and filtration is repeated several times. The crystal slurry obtained is finally carefully washed with a little methanol and dried. Repeated recrystallisation from benzene produces 2 - (2¹ - hydroxy - 3¹ - carbo - cyclohexyloxyamino - 5¹ - methylphenyl) - 5 - chlorobenztriazole. M.P. 197°.

The following compounds are obtained by an analogous process if instead of the 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - chlorobenztriazole, an equivalent amount of the corresponding aminophenyl benztriazole is used:

- 2 - (2¹ - hydroxy - 3¹ - carbocyclohexyloxy - amino - 5¹ - benzylphenyl) - 5 - methoxy - benztriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbocyclohexyloxy - amino - 5¹ - chlorophenyl) - 5 - chlorobenztriazole.

The end products mentioned can be used as UV absorbers and are suitable, depending on their solubility properties, as stabilisers for various synthetic materials.

EXAMPLE 13

The moist azo dyestuff obtained as filter residue on coupling 13.8 parts of diazotised *o*-nitroaniline and 29.8 parts of 2 - *p* - chlorobenzene sulphonamido - 4 - methylphenol, 300 parts by volume of 3 N caustic soda lye and 25 parts of zinc dust are stirred together at 0—5° until, after the zinc dust has settled, the colour of the solution has become yellow-green. The whole is stirred for another 15 minutes at 25° and, after cooling to 0°, the reaction mixture is made acid to congo paper with 30% by weight hydrochloric acid. The product is filtered off under suction, washed well with water and recrystallised from glacial acetic acid/dimethyl formamide. The 2 - (2¹ - hydroxy - 3¹ - *p* - chlorobenzosulphonamido - 5¹ - methylphenyl) - benztriazole melts at 234°.

On using 3 - nitro - 4 - aminobenzene sulphonic acid methyl amide instead of the *o*-nitroaniline, 2 - (2¹ - hydroxy - 3¹ - *p* - chloro-

benzene sulphonamido - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid methylamide is obtained by the same process.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 14

13.5 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methoxyphenyl) - 5 - methyl - benztriazole (M.P. 175°; produced according to Example 1 from 2 - (2¹ - hydroxy - 5¹ - methoxyphenyl) - 5 - methyl - benztriazole (M.P. 110°), and 5.2 parts of phenyl isocyanate in 130 parts of technical xylene mixture (B.P. 134—150°) are refluxed for 1.5 hours. The reaction mixture is cooled well and the 2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - amino - 5¹ - methoxyphenyl) - 5 - methyl - benztriazole obtained in crystalline form is filtered off under suction. Recrystallised from a mixture of glacial acetic acid/chlorobenzene, a product is obtained which melts at 231°.

By an analogous process on using an equivalent amount of a corresponding aminophenyl benztriazole instead of the 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methoxyphenyl) - 5 - methyl - benztriazole mentioned above, the following products are obtained:

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - benzylamino - 5¹ - cyclohexylphenyl) - 5 - chlorobenztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - amino - 5¹ - methylphenyl) - 5 - carbomethoxy - benztriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 15

The moist azo dyestuff, obtained by coupling 23.0 parts of diazotised 4 - amino - 3 - nitrobenzene ethyl sulphone and 26.5 parts of 2 - β - carboxypropionylamino - 4 - tert. butylphenol (obtained from 2 - amino - 4 - tert. butylphenol and succinic acid anhydride), 300 parts by volume of 3 N caustic soda lye and 25 parts of zinc dust are stirred together at 0—5° until the original blue-violet colour has completely changed to yellow. The reaction mixture is then acidified at 0° with concentrated hydrochloric acid until a congo blue reaction is obtained, whereupon it is filtered. The filter residue is taken up in cold 2 N caustic soda lye and zinc sludge is filtered off. Acidification with 10% by weight hydrochloric acid produces 2 - (2¹ - hydroxy - 3¹ - β - carboxypropionylamino - 5¹ - tert. butylphenyl) - benztriazole - 5 - ethyl sulphone. After repeated recrystallisation from methanol, it melts at 202°.

On saponifying 2 parts of the product obtained by refluxing with 5 parts of constant boiling hydrobromic acid and 10 parts of glacial acetic acid, removing the glacial acetic

acid by steam distillation and neutralising the hydrobromide formed, 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - tert. butylphenyl) - benztriazole - 5 - ethyl sulphone is obtained. It melts at 195° and can be converted by acylation into other acyl derivatives.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 16

12 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole, 50 parts of dry xylene mixture (B.P. 134—150°) and 6.6 parts of dimethyl aniline are stirred. A solution of 7.7 parts of *p* - toluic acid chloride in 100 parts of xylene mixture is added dropwise to the suspension obtained while stirring well at room temperature. On completion of the addition of the acylating agent, the mixture is slowly heated and kept for 45 minutes under reflux. The solvent is then removed with steam from the reaction mixture obtained and the 2 - (2¹ - hydroxy - 3¹ - *p* - methylbenzoyl - amido - 5¹ - methylphenyl) - benztriazole formed is isolated by filtering off from the aqueous phase. After washing well with 1 N hydrochloric acid and water, the product is dried and repeatedly recrystallised from methyl cellosolve. ("Cellosolve" is a Registered Trade Mark). It then melts at 210°.

The following products are obtained in the same manner on using corresponding aminophenylbenztriazole instead of the 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole:

2 - (2¹ - hydroxy - 3¹ - *p* - methylbenzoyl - amino - 4¹,5¹ - dimethylphenyl) - 5 - chlorobenztriazole,

2 - (2¹ - hydroxy - 3¹ - *p* - methylbenzoyl - amino - 5¹ - methylphenyl) - 5,6 - dichlorobenztriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic substances.

EXAMPLE 17

12 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole, 50 parts of chlorobenzene and 6.6 parts of dimethyl aniline are stirred together. A solution of 8.7 parts of *o* - chlorobenzoyl chloride in 50 parts of chlorobenzene is added dropwise while stirring well at room temperature. On completion of the addition, the mixture is slowly brought to the boil under reflux and refluxed for half an hour. The reaction mixture is cooled, 10 parts of glacial acetic acid are added and all the chlorobenzene is distilled off by steam distillation. The crystalline 2 - (2¹ - hydroxy - 3¹ - *o* - chlorobenzoylamino - 5¹ - methylphenyl) - benztriazole is filtered off from the aqueous suspension, washed well with 0.5 N hydrochloric acid and water and then dried under water jet vacuum. After repeated re-

crystallisation from methyl cellosolve, it melts at 211°.

If, instead of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole, the equivalent amount of the corresponding benztriazole derivative is used, then the following products are obtained:

2 - (2¹ - hydroxy - 3¹ - *o* - chlorobenzoyl - amino - 5¹ - cyclohexylphenyl) - 5 - carboxy - benztriazole,

2 - (2¹ - hydroxy - 3¹ - *o* - chlorobenzoyl - amino - 4¹ - chloro - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - *o* - chlorobenzoyl - methylamino - 5¹ - tert. butylphenyl) - benztriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic substances.

EXAMPLE 18

5.4 Parts of 2 - (2¹ - hydroxy - 5¹ - methylphenyl) - benztriazole - 5 - carboxylic acid (M.P. 255°; produced by coupling diazotised 4 - amino - 3 - nitrobenzoic acid and *p* - cresol and then closing the ring under alkaline conditions by reduction with zinc dust analogously to Example 2) are dissolved in 40 parts by volume of concentrated sulphuric acid. A mixture of 1.6 parts by volume each of concentrated nitric acid and water is added dropwise to this solution and the resultant solution is stirred for 1.5 hours at room temperature. The reaction mixture is then poured, while stirring well, onto ice. The 2 - (2¹ - hydroxy - 3¹ - nitro - 5¹ - methylphenyl) - 5 - carboxy - benztriazole which precipitates is filtered off under suction and washed well with water. Recrystallisation twice from glacial acetic acid produces a pure product which melts at 252°.

3.5 Parts of the above nitro compound are dissolved hot in a mixture of 10 parts by volume of 2 N caustic soda lye and 60 parts of water. This solution is quickly poured at 60° into a solution of 15 parts of sodium hydrosulphite in 100 parts of water whereupon the mixture formed is stirred for 45 minutes at 70—80°. After cooling to room temperature, the reaction mixture is acidified with 2 parts by volume of glacial acetic acid (red to litmus paper) and stirred overnight. The 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - carboxybenztriazole which precipitates is filtered off under suction and recrystallised twice from methyl cellosolve. The pure product melts under decomposition at 281—284°.

1.7 Parts of the above amino compound in 150 parts by volume of chlorobenzene and 0.60 parts of succinic acid anhydride are refluxed for 2 hours. The chlorobenzene is then removed from the reaction product by steam distillation. The 2 - (2¹ - hydroxy - 3¹ - β - carboxypropionylamino - 5¹ - methylphenyl) - 5 - carboxy - benztriazole obtained is

repeatedly recrystallised from methyl cellosolve whereupon it melts at 244°.

The 2 - (2¹ - hydroxy - 3¹ - carboxypropionylamino - 5¹ - methylphenyl) - 5 - carboxy - benztriazole obtained is esterified with ethanol or butanol using hydrochloric acid in gaseous form as catalyst to form 2 - (2¹ - hydroxy - 3¹ - carboethoxypropionylamino - 5¹ - methylphenyl) - 5 - carboethoxy - benztriazole or 2 - (2¹ - hydroxy - 3¹ - carbobutoxypropionylamino - 5¹ - methylphenyl) - 5 - carbobutoxy - benztriazole respectively.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 19

3.6 Parts of 2 - (2¹ - hydroxy - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid butylamide (M.P. 152°; produced by coupling diazotised 4 - amino - 3 - nitrobenzene sulphonic acid butylamide and *p* - cresol and closing the ring of the azo dyestuff obtained by zinc dust reduction under alkaline conditions) are dissolved hot in 160 parts by volume of glacial acetic acid. This solution is cooled as quickly as possible to 30° and a mixture of 0.8 parts by volume each of concentrated nitric acid and water is added dropwise. The mixture obtained is stirred overnight at room temperature and then 300 parts of water are added. The 2 - (2¹ - hydroxy - 3¹ - nitro - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid butylamide which precipitates is filtered off and recrystallised from ethanol/glacial acetic acid. M.P. 161°.

The suspension of 2 parts of the nitro compound described above in 100 parts by volume of methyl cellosolve is hydrogenated at room temperature under normal pressure using 0.2 parts of Raney nickel as catalyst. When the calculated amount of hydrogen has been taken up the hydrogen is displaced by nitrogen, the hydrogenation product is heated to 90—100° and the Raney nickel is filtered off hot using Hiflow (under a nitrogen blanket to prevent ignition of the possibly pyrophoric Raney nickel), and the Raney nickel is washed with hot methyl cellosolve. ("Hiflow" is a Registered Trade Mark). 200 Parts by volume of water are added to the clear filtrate and the 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid butylamide which precipitates is filtered off under suction. After drying, it is recrystallised twice from ethanol and then melts at 215°.

4 Parts of the amino compound described above, 100 parts by volume of chlorobenzene and 1.5 parts of succinic acid anhydride are refluxed for 2 hours. The chlorobenzene is removed from the reaction mixture by steam distillation. The 2 - (2¹ - hydroxy - 3¹ - β - carboxypropionylamino - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid butylamide so

obtained is purified by recrystallisation, e.g. from methanol, and then melts at 200°.

The following products are obtained in the same way on using an equivalent amount of the corresponding amino - phenylbenztriazole instead of the sulphonic acid butylamide derivative mentioned:

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - amino - 5¹ - chlorophenyl) - benztriazole - 5 - sulphonic acid cyclohexylamide,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - amino - 5¹ - ethylphenyl)benztriazole - 5 - sulphonic acid allylamide,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - amino - 4¹,5¹ - dimethylphenyl) - benztriazole - 5 - sulphonic acid benzylamide,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - cyclohexylamino - 5¹ - methylphenyl) - 5 - sulphonic acid diethylamide,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - butylamino - 4¹,5¹ - dimethylphenyl) - benztriazole - 5 - sulphonic acid allylmidide,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionyl - amino - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid benzylamide.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 20

13 Parts of methane sulphochloride are added dropwise at about 80° to 24 parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - benztriazole, 500 parts by volume of glacial acetic acid, 15 parts of sodium acetate and 20 parts of water. The mixture, which is opaque due to separation of sodium chloride is then refluxed for 1 hour while stirring well. 800 Parts of water are slowly added while the mixture is still hot, it is then cooled and filtered. The residue consisting of 2 - (2¹ - hydroxy - 3¹ - methane sulphonylamino - 5¹ - methylphenyl) - benztriazole is recrystallised several times from glacial acetic acid and then melts at 249°.

The following products are obtained by an analogous process using the equivalent amount of the corresponding acid chloride instead of the methane sulphochloride:

2 - (2¹ - hydroxy - 3¹ - cyclohexane sulphonic acid amido - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - allylsulphonic acid amido - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - benzylsulphonic acid amido - 5¹ - methylphenyl) - benztriazole, and

2 - (2¹ - hydroxy - 3¹ - butane sulphonic acid amido - 5¹ - methylphenyl) - benztriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 21

16 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - methoxybenztriazole (M.P. 147°, then solidifies and then melts at 164°; produced from 2 - (2¹ - hydroxy - 5¹ - methylphenyl) - 5 - methoxybenztriazole — M.P. 125° — by nitration and reduction according to Example 1), 200 parts by volume of chlorobenzene and 7 parts of phenyl isocyanate are refluxed for 1 hour. The chlorobenzene is removed from the reaction mixture by steam distillation. The 2 - (2¹ - hydroxy - 3¹ - phenylcarbamoylamino - 5¹ - methylphenyl) - 5 - methoxybenztriazole which separates is recrystallised several times from glacial acetic acid and then has an unsharp melting point at 206°.

The following products are obtained in the same way using an equivalent amount of the corresponding aminophenyl - benztriazole instead of the 5 - methoxy derivative:

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - octylamino - 5¹ - tert. butylphenyl) - 5 - methylbenztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - β - carboxyethylamino - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - cyclopentylamino - 5¹ - methylphenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - phenylcarbamoyl - β - carboethoxyethylamino - 5¹ - phenylphenyl) - benztriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 22

13 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - chlorophenyl) - benztriazole and 6.7 parts of phenyl isothiocyanate in 100 parts by volume of ethylene glycol monomethyl ether are refluxed for 2 hours. After cooling, the precipitate is filtered off and crystallised from ethylene glycol monomethyl ether. 12.5 Parts of 2 - (2¹ - hydroxy - 3¹ - phenyl - thiocarbamoyl - amino - 5¹ - chlorophenyl) - benztriazole are obtained. M.P. 276°.

If butyl mustard oil is used instead of phenyl isothiocyanate, then 2 - (2¹ - hydroxy - 3¹ - butyl - thiocarbamoylamino - 5¹ - chlorophenyl) - benztriazole is obtained.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 23

27 Parts of 2 - (2¹ - hydroxy - 3¹ - amino - 5¹ - methylphenyl) - 5 - chlorobenztriazole, 1000 parts by volume of chlorobenzene and 20 parts of dimethyl aniline are stirred together. 20 Parts of chlorocarbonic acid benzyl ester

are added dropwise to the suspension formed and, after slowly heating, the whole is refluxed for 1 hour. The blue reaction mixture is allowed to cool and is then filtered. The filtrate is concentrated in vacuo and the residue is combined with the first residue and then washed carefully with a little methanol which contains a few drops of concentrated hydrochloric acid. After drying, the product is recrystallised three times from benzene. The 2 - (2¹ - hydroxy - 3¹ - carbobenzyloxy - amino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole so concentrated melts then at 168°.

The following products are obtained by the same method on using an equivalent amount of the corresponding chlorocarbonic acid ester or chlorocarbonic acid amide instead of the benzyl ester:

- 2 - (2¹ - hydroxy - 3¹ - carbophenoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbo - *p* - chlorophenoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbo - β - chloroethoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbo - β - butylmercaptoethoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - (N - methylcyclohexyl - carbamoylamino) - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - (N - pentamethylene - carbamoylamino) - 5¹ - methylphenyl) - 5 - chlorobenzotriazole,
- 2 - (2¹ - hydroxy - 3¹ - carbo - β - methoxyethoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 24

3.2 Parts of 2 - (2¹ - hydroxy - 3¹ - chloroacetamido - 5¹ - methylphenyl) - benzotriazole (M.P. 201°) and 2 parts of diethylamine in 100 parts by volume of ethanol are refluxed for 12 hours. After cooling, the 2 - (2¹ - hydroxy - 3¹ - diethylaminoacetamido - 5¹ - methylphenyl) - benzotriazole formed is filtered off under suction and recrystallised from ethylene glycol monomethyl ether. It melts at 247°.

The following products are obtained by the same method on using equivalent amount of morpholine or N - methyl - cyclohexylamine instead of diethylamine:

- 2 - (2¹ - hydroxy - 3¹ - morpholino - acetamido - 5¹ - methylphenyl) - benzotriazole, or
- 2 - (2¹ - hydroxy - 3¹ - N - methylcyclohexylamino - acetamido - 5¹ - methylphenyl) - benzotriazole.

The end products mentioned can be used as UV absorbers and, depending on their solubility properties, are suitable as stabilisers for various synthetic materials.

EXAMPLE 25

UV dense cellulose acetobutyrate films were produced by drawing a solution of 150 parts of Cellit BF—900 (cellulose - acetobutyrate of Farbenfabriken Bayer A.G., Leverkusen, Germany), 20 parts of dibutyl phthalate, 800 parts of acetone and 0.35 parts of 2 - (2¹ - hydroxy - 3¹ - benzoylamino - 5¹ - methylphenyl) - benzotriazole onto glass. ("Cellit" is a Registered Trade Mark).

After the solvent had been evaporated off, a colourless film of 0.4 mm strength was obtained which, for all practical purposes, absorbs all UV light in the wavelengths under 380 m μ and is excellently suitable as a protective film, for example, for use in shop windows.

Films having similar absorption powers are obtained if, instead of the compound used, a similar amount of 2 - (2¹ - hydroxy - 3¹ - carbomethoxyamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole or 2 - (2¹ - hydroxy - 3¹ - methane sulphonic acid amido - 5¹ - methylphenyl) - benzotriazole is used.

Very similar films which are also UV dense for all practical purposes are obtained in the same way but on using other cellulose esters, i.e. cellulose acetate and cellulose propionate.

EXAMPLE 26

100 parts of the marketed liquid polyester resin consisting of 70% of a polycondensate of maleic acid, phthalic acid and ethylene glycol and 30% of styrene, are mixed with 0.1 parts of 2 - (2¹ - hydroxy - 3¹ - capryloylamino - 5¹ - methylphenyl) - 5 - chlorobenzotriazole and 1 part of benzoyl peroxide and the mixture is poured into a form and cured by heating for 3 hours at 80°. The 2 mm thick, colourless, transparent polyester resin plate formed absorbs all UV light in the wavelengths of less than 380 m μ and can be used as UV filter. Such polyester plates are suitable as roofing material.

Polyester resin plates stabilised against discolouration due to the effect of light are produced in an analogous manner if, instead of styrene, an equivalent amount of methylmethacrylate is used. If instead of maleic acid, 1,4,5,6,7,7 - hexachlorobicyclo - 5 - heptene - 2,3 - dicarboxylic acid (Het-acid) is used, then flame resistant polyester resins which absorb UV light well are obtained.

EXAMPLE 27

A mixture consisting of 65 parts of polyvinyl chloride (Lonza A.G. Basle), 32 parts of dioctyl phthalate, 2 parts of barium/cadmium laurate, and 0.5 parts of 2 - (2¹ - hydroxy - 3¹ - capryloylamino - 5¹ - methylphenyl) - benzotriazole,

are calendered on a set of two mixing rollers at 150° into a film of 0.1 mm strength. It absorbs UV light and can be used as packing material for UV-sensitive materials. Its transmission of UV light at 360 mμ is less than 6%.

Similar results are obtained if, instead of the benztriazole compound mentioned, 0.5 parts of:

2 - (2¹ - hydroxy - 3¹ - benzoylamino - 5¹ - methylphenyl) - 5 - carbobutoxy - benztriazole,

2 - (2¹ - hydroxy - 3¹ - β - carboxypropionylamino - 5¹ - tert. butylphenyl) - benztriazole - 5 - ethyl sulphone, or

2 - (2¹ - hydroxy - 3¹ - β - carboisopropoxy - propionylamino - 5¹ - methylphenyl) - benztriazole - 5 - sulphonic acid butylamide, are used.

In the same way, copolymers of polyvinyl chloride and polyvinyl acetate can be worked up in the UV dense films.

EXAMPLE 28

100 Parts of polyethylene powder (DFD 4400 of Union Carbide International Chemical Company, 30 East 42nd Street, New York, USA) are mixed with 0.25 parts of 2 - (2¹ - hydroxy - 3¹ - carbomethoxybenzyl - amino - 5¹ - methylphenyl) - benztriazole and the mixture is blown from an extruder into a film of about 0.06 mm thickness.

The film absorbs UV light and can be used as a protective layer, for example, for covering greenhouses.

If, instead of polyethylene, polypropylene (Profax 6512 of Hercules Powder Co., Wilmington, Delaware, USA) is used then a UV absorbant polypropylene film of high transparency in the visible range is obtained by extrusion through a slit dye at 250—270° ("Profax" is a Registered Trade Mark).

Films having very similar UV absorbant properties are obtained if 2 - (2¹ - hydroxy - 3¹ - o - chlorobenzoylmethylamino - 5¹ - tert. butylphenyl) - benztriazole is used as light stabiliser.

EXAMPLE 29

100 Parts of granulated Nylon 66 (produced by condensation of hexamethylenediamine and adipic acid in molar ratio 1:1 at about 265° while excluding oxygen) and 0.5 parts of 2 - (2¹ - hydroxy - 3¹ - p - toluene sulphonamido - 5¹ - methylphenyl) - benztriazole are mixed in the dry state and extruded into a continuous film. The film absorbs UV light and is suitable as UV absorbant packing material. A similar result is obtained if, instead of Nylon 66, Nylon 6 or 11 or the mixed condensate 6/10 is used.

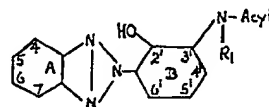
Similar results are also obtained if, instead of the benztriazole compound mentioned, 0.7 parts of 2 - (2¹ - hydroxy - 3¹ - phenylcarbamoylamino - 5¹ - benzylphenyl) - benztriazole is used.

EXAMPLE 30

100 Parts or methyl methacrylate, 0.1 parts of 2 - (2¹ - hydroxy - 3¹ - carbomethoxybenzylamino - 5¹ - methylphenyl) - benztriazole and 0.2 parts of lauroyl peroxide as polymerisation accelerator are well mixed and polymerised between two glass plates at 70° into a plate 2mm thick. The plate has a light transmission of less than 1% at 350 mμ. This transmission is substantially unchanged even when a sample of this plate is exposed for 1000 hours in a fadeometer. In this way, using suitable glass plates, UV dense polymethacrylate windows can be produced which, for example, can be used in the construction of aeroplanes.

WHAT WE CLAIM IS:—

1. Process for the production of substituted 2 - (2¹ - hydroxyphenyl) - benztriazole compounds, characterised by heating a 2 - (2¹ - hydroxyphenyl) - benztriazole compound containing an acylatable amino group in the 3¹ - position with an acylating agent to form a compound of the general formula I



wherein "Acyl" represents an organic acyl radical as hereinbefore defined, and R₁ represents hydrogen or alkyl, alkenyl, cycloalkyl or aralkyl radical which are possibly substituted by a carboxyl or carboxylic acid ester group whilst R₁ and "acyl" together with the amino nitrogen atom can form a ring and in this case R₁ is a carbonyl group or a methylene group possibly substituted by alkyl groups, and wherein the nucleus A can be substituted in the 4-, 5- and 6-positions by alkyl alkoxy, carboxy, carboxylic acid ester, carboxylic acid amide, sulphonic acid amide and alkylsulphonyl groups or by halogens, and the nucleus B can be substituted in the 4¹- and 5¹-positions by alkyl, cycloalkyl, aralkyl and aryl groups, alkoxy groups or by halogens.

2. Process for the production of substituted 2 - (2¹ - hydroxyphenyl) - benztriazole compounds characterised by oxidising, by known methods, a 2 - amino - 2¹ - hydroxy - 3¹ - acylamino - 1,1¹ - azobenzene compound to form a compound of formula I.

3. Process for the production of substituted 2 - (2¹ - hydroxyphenyl) - benztriazole compounds characterised by reducing by methods known per se, a 2 - nitro - 2¹ - hydroxy - 3¹ - acylamino - 1,1¹ - azobenzene compound to form a compound of formula I.

4. Process for the production of substituted 2 - (2¹ - hydroxyphenyl) - benztriazole compounds, characterised by dealkylating by

- methods known per se the alkoxy group in a 2 - (2¹ - alkoxy - 3¹ - acylaminophenyl) - benztriazole compound or hydrolysing the acyloxy group by methods known per se in a 2 - (2¹ - acyloxy - 3¹ - acylaminophenyl) - benztriazole compound to form a compound of formula I.
- 5 5. A compound of the general formula I.
- 10 6. Manufacture of 2 - (2¹ - hydroxyphenyl)- benztriazole compounds according to claim 5 substantially as described with reference to any of the foregoing Examples 1 to 24.
- 15 7. 2 - (2¹ - hydroxyphenyl) - benztriazole compounds according to claim 5 whenever prepared or produced by the processes of manufacture particularly described.
8. A 2 - (2¹ - hydroxyphenyl) - benztriazole compound according to claim 5 as identified in any of the foregoing Examples 1 to 24.
9. Organic materials containing a compound of the general formula I. 20
10. Organic materials as claimed in claim 9 whenever obtained by a process hereinbefore particularly described.
11. Organic materials as claimed in claim 9 as hereinbefore described with reference to and as illustrated in the foregoing Examples 25 to 30. 25

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